INVESTIGATION OF SILVER NANOPARTICLES AS NOVEL CATALYSTS FOR HYPERGOLIC HYDROCARBON PROPELLANTS WITH HYDROGEN PEROXIDE

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ABSTRACT:

To replace commonly-used toxic and carcinogenic propellants like hydrazine and its derivates, we developed new hypergolic propellants for space propulsion. Hydrogen peroxide and kerosene are promising candidates for hypergolic propellants because of their relatively low toxicity and cost, appropriate storage properties and good propulsion performances. On basis of previous studies, we chose silver nanoparticles as heterogenic catalysts for hydrogen peroxide decomposition. Most important factor in this study was stabilisation of the nanoparticles in the fuel. For this, different capping agents were investigated as stabilising additives and also gelling of the fuels was considered. By variation of experimental parameters like size of the silver nanoparticles and adjustment of catalyst amount, we created an optimised hypergolic propellant mixture with high concentrated hydrogen peroxide as oxidiser. The IDT (ignition delay time) of a stabilised bipropellant with 5 wt% of catalyst was decreased to 18.6 ms ± 1.6 ms. With higher catalyst amounts (8 wt%), IDTs of even < 10 ms are reached.

1. Introduction

Investigation of advanced hypergolic propellants is essential, as they are deployed for a majority of space flight manoeuvres. These propellant combinations consist of two components – oxidiser and fuel – which spontaneously ignite upon contact. However, most of the hypergolic propellants used at the present time have a weighty disadvantage: fuels as hydrazine and its derivates like monomethyl hydrazine (MMH) or unsymmetrical dimethyl hydrazine (UDMH) in combination with dinitrogentetroxide (NTO) as oxidiser are toxic substances. Hydrazine, for example, is also categorised as carcinogenic and environmentally harmful and is therefore listed as substance of very high concern of the European REACH (Registration, Evaluation, Authorization of Chemicals) regulation. It is possible that a prohibition of hydrazine will be introduced in the EU, so research in alternative propellants is very urgent. [1]

Hydrogen peroxide and hydrocarbon fuels such as kerosene are promising candidates for advanced bipropellant combination – not only because of their good propulsion performances – but also because of positive qualities as low cost and toxicity as well as easy handling. [2-4] However, hypergolisation of this system is still a challenge. Building on our previous work, we chose silver nanoparticles as catalyst for hydrogen peroxide decomposition. [5]

Nanoparticles are outstanding catalysts because of their very large surface to volume ratio which leads to a vast increase of reactivity of nanosized particles compared to bulk material. [6] Part of the nanoparticles we utilised for this study were synthesised in the physical chemical laboratory by bottom-up synthesis methods. The characterisation was performed by dynamic light scattering, UV/Vis-spectroscopy as well as thermogravimetry and differential thermal analysis. Ignition delay times (IDTs) of hypergolic propellants were determined by drop-on-pool tests. Benchmark for these tests is the hypergolic propellant combination MMH/NTO, which has an IDT in the order of a millisecond. [7]

Key challenge in this study is the stabilisation of the nanoparticles in the selected fuels to prevent sedimentation and reach for homogeneous distribution of the particles. The aim is to create hypergolic propellants with ignition delay times as short as possible. For this, we tested different additives such as sodium dodecyl sulfate (SDS), cetrimonium bromide (CTAB) or oleylamine and investigated their quality as stabilising capping

agents. Within this context, the zeta potential of prepared dispersions was determined as a sign of stability.

Gelation of the fuels is chosen as an alternative stabilisation strategy. Gelled propellants have been extensively studied in the past years because of their benign properties; in this case the most important factor is that gelling prevents particle sedimentation in the fuel. [8]

2. SILVER NANOPARTICLES: SYNTHESIS AND CHARACTERISATION

Silver has proven to catalyse hydrogen peroxide very efficiently. In comparison to platinum and manganese dioxide, which are also known catalysts for peroxide decomposition, silver nanoparticles have shown even significantly better catalytic performance in hypergolic propellants. [5] Besides this, silver nanoparticles were chosen in this study because of their health- and environmentally friendliness combined with the fact, that they are easy to synthesise and commercially available.

Nanoparticles are defined as materials in a size range between 1 nm and 100 nm. The surface of a material is the catalytically active part, therefore small particles are much more effective catalysts than larger ones. Nanoparticles appear in a wide variety of different applications as they show very interesting optical, electrical, mechanical and magnetical properties. [6] One important aspect about nanoparticles is that capping agents play a principal role when handling them in dispersions. On the one hand, these surfactants are essential for synthesis processes as they affect size and shape of the particles. On the other hand, they are also responsible for the formation of long-term stable dispersions of particles in dispersants as they are able to prevent particle aggregation. The zeta potential ζ offers a physical variable to evaluate stability of such dispersions. It is defined as the electric potential at the shear plane of dispersed particles as shown in Fig. 1.

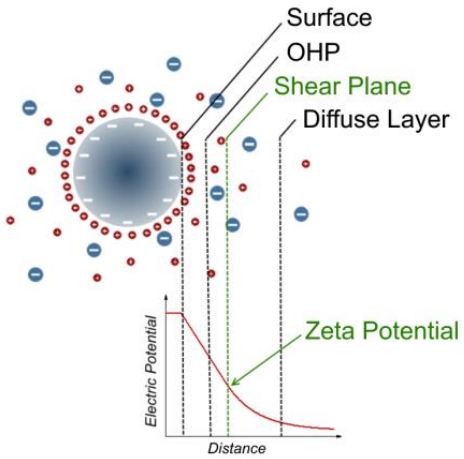

Figure 1. Schematic representation of the zeta potential on basis of the double layer model. OHP: Outer Helmholtz plane. [5]

This shear plane is the interface between a rigid inner layer of ions around a charged particle and a weaker outer layer. High absolute values ($\zeta \geq \pm 30$ mV) of the zeta potential characterise dispersions with highly repulsive interactions between the particles and therefore highly stable colloids. [9-13]

The different ways to increase the stability of dispersions can be divided into two groups.

- *Steric stabilisation* is obtained through coverage of the particle surfaces with sterically demanding ligands. Adsorptions of such surfactants result in a decreased mobility of the particles. Subsequently, entropy of the whole system is decreased, as an approximation of these particles is thermodynamically less favourable.
- *Electrostatic stabilisation* is based on an increase of the charge density at nanoparticle surfaces. This raises the potential energy barrier of the particle precipitation and the colloid is more stable. When both types are involved, the term *electrosteric stabilisation* is used. [13,14]

For quality and task-specific purposes, self-synthesised silver nanoparticles as well as purchased ones were utilised in this study. Synthesis of silver nanoparticles was carried out at the physically-chemical laboratory. A wet-chemically synthesis process (bottom-up synthesis) namely a *polyol method* was carried out. Silver ions in form of $AgNO_3$ (≥ 99.9 %, Carl Roth) were dissolved in ethylene glycol (> 99.5 %, Merck) which also functions as a reducing agent at higher temperatures (125 °C, heating rate approx.

6 K/min). In presence of the capping agent polyvinylpyrrolidone (PVP, M_w = 2 500 g/mol, pure, Carl Roth) silver nanoparticles were formed after 30 minutes. For purification, the nanoparticles were centrifuged (9 000 rpm) and redispersed in ethanol. This process was repeated two times. This synthesis is oriented towards [15]. Further substances include ethanol (pure, Carl Roth) sodium dodecyl sulfate (SDS, ≥99 %, Carl Roth) cetrimonium bromide (CTAB, high purity, VWR) and oleylamin (C18-content 80-90 %, Acros Organics) and were used without further purification.

3. EXPERIMANTAL SETUP

Fig. 2 shows the test setup which is used to determine the IDT of hypergolic propellant mixtures.

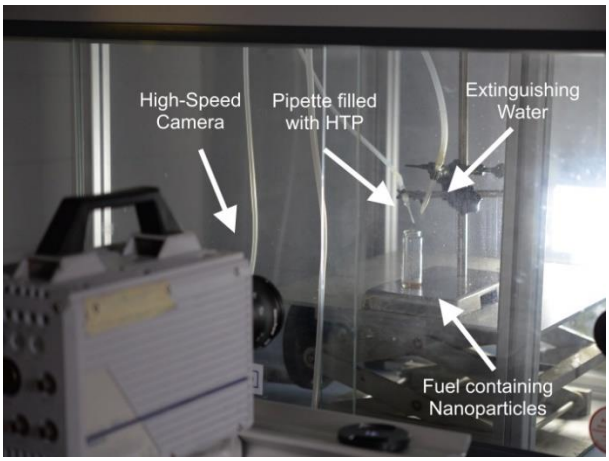

Figure 2: Drop test setup for determination of IDTs [5].

All experiments were performed in a fume hood with an additional protection screen at 25 °C. The oxidiser HTP (high test peroxide, ~ 97 %, drop size: 45.5 mg ± 1.29 mg) was dropped from a pipette, which was connected with a syringe. The fuel was located in a glass vessel. A separate quenching mechanism was installed for safety reasons. Two LED lamps were installed to improve lighting conditions. Drop tests were filmed by a high-speed camera with a recording speed of 3000 fps. The IDT was determined by analysing the videos frame per frame. Fig. 3 shows single sequences of an ignition event of a hypergolic propellant. The hydrogen peroxide drop approaches the fuel in the first picture and touches its surface in the second one. This is when the time span of the ignition delay starts. After mixing of the two components and steam generation, a first flame is observed in the third picture which indicates the end of the IDT span and results in a rapid propagation of the flame.

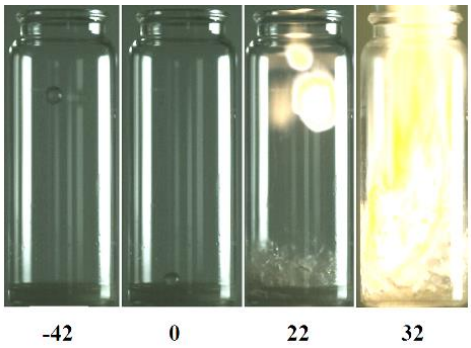

Figure 3: Ignition sequence of a hypergolic propellant with an IDT of 22 ms.

4. RESULTS AND DISCUSSION

4.1 Test series 0: First tests of the system

For test series 0 silver nanoparticles Ag^{P}_{nano} were used which were synthesised in the physical-chemical laboratory. The size of those as-prepared particles was determined to be 37.4 nm ± 10.4 nm by dynamic light scattering (DLS). Fig. 4 shows the size distribution of the synthesized particles.

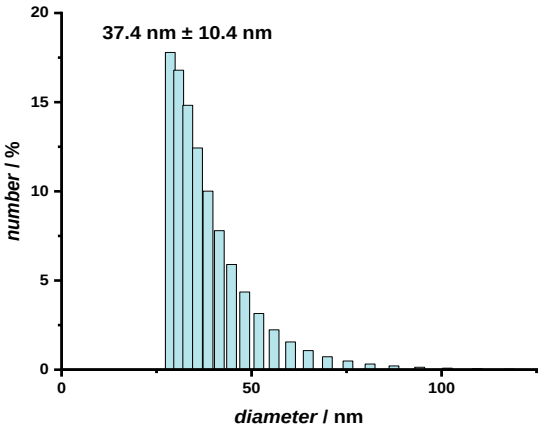

Figure 4. Size distribution of Ag^{P}_{nano} in water measured by dynamic light scattering.

An absorption spectrum was measured to verify size of the silver nanoparticles. Nanoparticles of certain transition metal nanoparticles show absorption bands in specific regions because of the plasmon resonance effect. [16] For silver particles, the absorption maximum is located between 400 nm and 530 nm and can therefore be detected by UV-Vis spectroscopy. With increasing particle size, the absorption maxima show a bathochromic shift. Fig. 5 presents the absorption spectrum of Ag^{P}_{nano} with a maximum at 407 nm, which underlines results of DLS measurement.

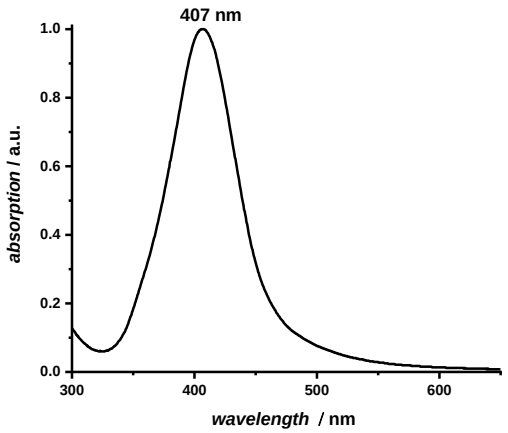

Figure 5: Absorption spectrum of synthesized Ag^{P}_{nano} in water.

A thermogravimetric analysis of Ag^{P}_{nano} was made to determine the amount of PVP polymer which is adsorbed on the surface of the nanoparticles (Fig. 6). The dispersant was removed in a drying chamber at 70 °C. The measurement was conducted under nitrogen to avoid particle oxidation.

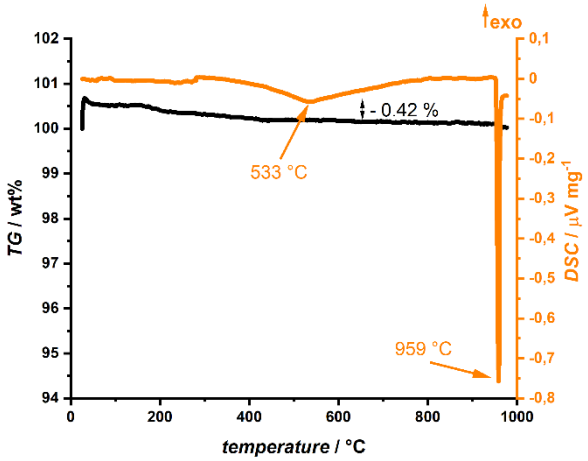

Figure 6. TG/DSC-diagram of Ag^{P}_{nano}. Measurement was conducted under nitrogen in an alumina crucible.

The fuel combination of this first test consisted of 68 wt% heptane, 24 wt% EtOH and 8 wt% Ag^{P}_{nano}. Heptane is used as kerosene substitute, but ignition behaviour is expected to be properly transferrable. Results of first drop tests are summarised in Tab. 1.

Table 1. Initial findings of drop tests of a hypergolic propellant combination.

	Test 1	Test 2	Average	Standard deviation
IDT [ms]	4.0	12.7	8.4	4.4

The very short IDTs in Tab. 1 show that silver nanoparticles are effective catalysts for this propellant mixture. But the ignition delay time measured in the second test is more than thrice as high as the one in the first test. This led to a very high standard deviation, which can be explained by sedimentation of the not-stabilised particles in the fuel. Yet, both ignition delay times are shorter than the ones we found in literature in comparable systems [4]. Therefore, the approach of stabilising silver nanoparticles in hydrocarbon fuels is a promising concept, which is adopted in the following work. Key challenge of this study is the stabilisation of nanoparticles for long-term stable fuels.

4.2 Investigation of the fuel behaviour with purchased silver nanoparticles

There are different routes to optimise stabilisation of the silver nanoparticles in hydrocarbon fuels. As synthesis in the physical-chemical laboratory is complex and time consuming, the following experiments in chapter 4.2. were conducted with commercial purchased silver nanoparticles. However, it turned out that the purchased particles we utilised in this study are not as effective catalysts as the ones synthesised in our laboratory. In the following test series, reduced amounts of catalyst were used than in the previous test series.

4.2.1 Test series 1: Comparison of different types of silver nanoparticles

Silver nanoparticles of five different sizes were purchased and tested as catalysts in the hypergolic propellant combination. The results of tests series 1 are summarised in Tab. 2.

Table 2. Details of test series 1 with average IDTs and standard deviations. Size according to the manufacturer's specification. Drop tests were performed with 5 wt% of catalyst in heptane with HTP.

Catalyst	No. of tests	Average IDT [ms]	Standard deviation [ms]
AgNP-P1 (20 nm)	4	178.7 [b]	30.4
AgNP-P2 (35 nm)	2	165.5	42.5
AgNP-P3 (20-40 nm)	2	538.5	8.5
AgNP-P4 (50-60 nm)	2	-	

AgNP-P3 (<100 nm)	2	471.5	67.5

[a]only 2 ignitions

Analysis of this test series revealed enormous differences between the examined silver nanoparticle catalysts. One silver nanoparticle species – AgNP-P4 – did not cause any ignition. As AgNP-P2 reached the shortest average IDT, further studies were carried out with this catalyst.

4.2.2 Test series 2: Investigation on different amounts of ethanol

In test series 2, impact of additional ethanol on ignition behaviour of the heptane-based propellant was investigated. Tab. 3 summarises results of the drop tests with 0, 10 and 25 wt% of ethanol, respectively.

Table 3. Details of test series 2 with average IDTs and standard deviations. Drop tests were performed with 5 wt% of catalyst with HTP.

Amount of ethanol [wt%]	No. of tests	Average IDT [ms]	Standard deviation [ms]
0	2	165.5	42.5
10	3	75.2	5.2
25	3	69.2	6.4

Test series 2 shows, that IDTs are decreased through by the addition of ethanol. This effect is very pronounced by comparison of 0 and 10 wt% of ethanol. More ethanol did not lead to a significant greater decrease. As ethanol had an adverse effect on the I_{sp} of the hypergolic propellant, further studies were conducted with 10 wt% of ethanol in the fuel.

4.2.3 Test series 3: Comparison of different gelling agents (GA)

In order to improve long-term-stabilisation of nanoparticles, gelling of the fuel was considered. Fig. 7 shows an example of a gel which contains silver nanoparticles. Tab. 4 presents results of drop tests of fuels with three different gelling agents.

Figure 7. Heptane-based fuel gelled with GA-2.

Table 4. Details of test series 3 with average IDTs and standard deviations. Drop tests with HTP were performed with 5 wt% of catalyst in a heptane-based fuel with 10 wt% ethanol. Percentage of gelling agent was 7 wt%, respectively.

Gelling agent	No. of tests	Average IDT [ms]	Standard deviation [ms]
none	3	75.2	5.2
GA-1	2	no ignition	-
GA-2	3	183.9	18,2
GA-3	3	no ignition	-

Outcome of test series 3 is, that gelation has a negative impact on the IDT in this type of system. In two cases, no ignition was observed. In case of GA-2, the IDT was significantly higher than in the system without gelling agent. Therefore, the next approach is based on another kind of stabilisation of nanoparticles in the fuel.

4.2.4 Test series 4: Comparison on different stabilising “capping agents”

As gelling led to increased IDTs or even prevented igntion, capping agents were tested as an alternative approach. In order to find suitable substances, a selection of capping agents was solved in heptane to study their solubility, as shown in Fig. 8.

Figure 8. *Different capping agents in heptane.*

As a final result of the pre-tests, SDS, CTAB and oleylamine were chosen. Each heptane-based fuel in Fig. 9 contains 5 wt% of catalyst consisting of 90 wt% silver nanoparticles with 10 wt% stabilising capping agents, respectively.

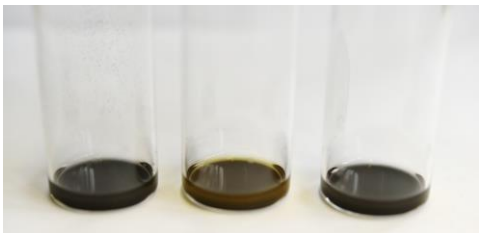

Figure 9. Silver nanoparticles stabilised with SDS, CTAB and oleylamine (from the left to the right) in a heptane-based fuel with 10 wt% of ethanol.

Again, drop tests with hydrogen peroxide were carried out. The findings are summarised in Tab. 5.

Table 5. Details of test series 4 with average IDTs and standard deviations. Drop tests with HTP were performed with 5 wt% of catalyst in a heptane-based fuel with 10 wt% ethanol.

Capping Agent	No. of tests	Average IDT [ms]	Standard deviation [ms]
none	3	75.2	5.2
SDS	2	no ignition	-
CTAB	3	no ignition	-
oleylamine	3	36.8	0.6

The addition of SDS and CTAB prevented ignition. The fuels with additional oleylamine, on the contrary, showed ignition delay times almost half as short as the ones without capping agent. The clearly lower standard deviation of the drop tests with oleylamine is also remarkable, as this stands for a stabilised fuel with homogenously distributed nanoparticles.

With oleylamine, a suitable capping agent for this hypergolic propellant combination was found which improves the performance of the fuel significantly. The next chapter 4.3 describes the application of the previous findings on the initial system with Ag^{P}_{nano}.

4.3 Optimising the initial system with Ag^{P}_{nano}

4.3.1 Test series 5: Investigation on different amounts on ethanol

To verify the comparability of Ag^{P}_{nano} with the previously tested ones, study with different heptane-ethanol-ratio was repeated without additional capping agents. This time, only 1 wt% of catalyst was used. The results of test series 5 are listed in Tab. 6.

Table 6. Details of test series 5 with average IDTs and standard deviations. Drop tests were performed with 1 wt% of catalyst with HTP.

Amount of ethanol [wt%]	No. of tests	Average IDT [ms]	Standard deviation [ms]
0	3	52.5	10.6
10	3	26.1	3.1
25	3	29.6	1.5

Fig. 10 illustrates, that small amounts of ethanol are sufficient for a significant decrease of the ignition delay time. Remarkably, in this test series the samples with 25 wt% of ethanol showed a slightly higher IDT than the one with 10 wt%.

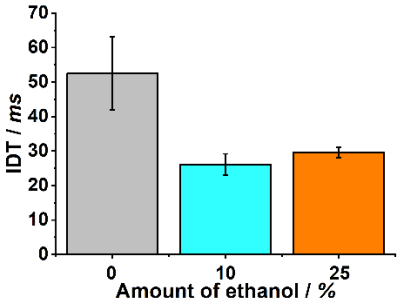

Figure 10. Average IDTs and standard deviations of test series 5. Drop tests were performed with 1 wt% of catalyst with HTP.

4.3.2 Test series 6: Investigation on different stabilising agents

To optimise the fuel in a last step, the stabilising capping agents were added again. The results in Tab. 7 confirm the findings of test series 4:

Table 7. Details of test series 6 with average IDTs and standard deviations. Drop tests with HTP were performed with 5 wt% of catalyst in a heptane-based fuel with 10 wt% ethanol. Zeta Potentials were measured in ethanol.

Capping Agent	No. of tests	Zeta potential ζ [mV]	Average IDT [ms]	Standard deviation [ms]
none	3	-5.83	21.2	3.6
SDS	2	-6.94	153.0[b]	-

CTAB	3	-32.85	no ignition	-
oleylamine	3	-14.55	18.6	1.6

[b]only one igntition

Again, fuels with CTAB as stabilising capping agents didn't ignite. In case of SDS, one ignition was observed but with a relatively long IDT of 153.0 ms. Once more, oleylamine-stabilised particles led to a decreased IDT of 18.6 ms compared to the particles without stabilisation (Fig. 11).

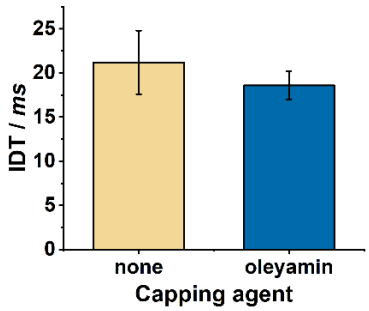

Figure 11. Average IDTs and standard deviations of test series 6. Drop tests with HTP were performed with 5 wt% of catalyst in a heptane-based fuel with 10 wt% ethanol.

Zeta potentials of the nanoparticles with these capping agents were determined as criterion for stabilisation of the nanoparticles. Fig. 12 shows the measurement of oleylamine stabilised silver nanoparticles in ethanol. Oleylamine-stabilised dispersions have a significantly reduced negative zeta potential of -14.55 mV than the pure fuel (-5.83 mV) and are therefore more stable, which makes a longer storage of the fuel possible. Zeta potentials of the fuels with CTAB stabilised particles are even higher, but this capping agent prevents ignition and is therefore not suitable.

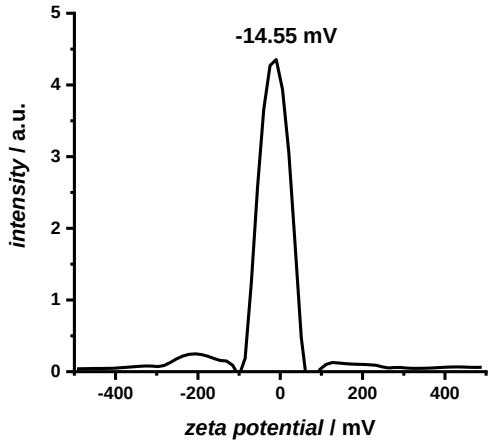

Figure 12. Zeta potential of Ag^{P}_{nano} stabilised with oleylamine in ethanol.

5. CONCLUSION

The combination of hydrogen peroxide and kerosene is a promising "green" alternative for state-of-the-art hypergolic propellants. In this study, silver nanoparticles have proven to be effective catalysts for this system as they led to very low ignition delay times. Self-synthesised as well as purchased silver nanoparticles were tested, whereas the freshly prepared particles reached significantly lower IDTs. To prevent sedimentation of nanoparticles in the fuels, two different approaches were considered. First, gelling of the fuels was tested, but it turned out that this was not suitable for the system. Second, capping agents were used to stabilise the nanoparticles in the fuels. With oleylamine, we found a capping agent for this propellant combination which is able to stabilise the silver nanoparticles in the fuel – not only without a negative impact on the IDTs – but even with a shift to lower IDTs, which can be attributed to a more homogeneous distribution of the nanoparticles. Measurement of the zeta potential confirmed the successful stabilisation of the nanoparticles. The ignition delay time of an oleylamine-stabilised bipropellant with 5 wt% of catalyst reached 18.6 ms ± 1.6 ms. Initial tests showed, that with higher catalyst amounts (8 wt%), IDTs of even < 10 ms are possible.

6. ACKNOWLEDGEMENT

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7. REFERENCES

[1] Malm, J. (2011). Inclusion of substances of Very High Concern in the Candidate List, Helsinki: European Chemicals Agency (ECHA).

[2] Connell T.L., Risha, G.A., Yetter, R.A. & Natan, B. (2018). Ignition of Hydrogen Peroxide with Gel Hydrocarbon Fuels. *Journal of Propulsion and Power*, **34**(1), 170-181.

[3] Cong, Y., Zhang, T., Li, T., Sun, J., Wang, X., Ma, L., Liang, D., & Lin, L. (2004). Propulsive Performance of a Hypergolic H2O2/Kerosene Bipropellant. *Journal of Propulsion and Power*, **24**(1), 83-86.

[4] Yuan, T., Chen, Y. & Zhou, J. (2018). The Auto-Ignition of Kerosene-Based Synthetic Fuel/ Hydrogen Peroxide Propellants and Its Injector Design. *AIAA Propulsion and Energy Forum,* Cincinnati, Ohio.

[5] Ricker, S., Kurilov, M., Freudenmann, D., Kirchberger, C., Hertel, T., Ciezki, H. K. & Schlechtriem, S. (2019). Novel gelled fuels containing nanoparticles as hypergolic

bipropellants with HTP. *Proceedings of 8th European Conference for Aeronautics and Space Sciences (EUCASS 2019)*, Madrid, Spain.

[6] Astruc, D., Lu, F., & Aranzaes J. (2005) Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angew. Chem. Int. Ed.* **44**, 7852-7872.

[7] Chambreau, S. D., Schneider, S. Rosander, M., Hawkins, T., Gallegos, C. J. Pastewait, M. F., Vaghjiani, G. L. (2008). Fourier Transform Infrared Studies in Hypergolic Ignition of Ionic Liquids. *J. Phys. Chem. A*. **112**, 7816–7824.

[8] Kirchberger, C., Kurilov, M., Stiefel, A., Freudenmann, D. and Ciezki, H. K. (2019). Investigations on Rheology, Spray and Combustion Processes of Gelled Propellants at DLR Lampoldshausen. *Proceedings of 8th European Conference for Aeronautics and Space Sciences (EUCASS 2019)*, Madrid, Spain.

[9] Boström, M., Williams, D. R. M. & Ninham, B. W. (2001). Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems. *Phys. Rev. Lett.* **87**(16), 168103.

[10] Israelachvili, J. N. (2011) Van der Waals Forces. Intermolecular and Surface Forces. *Elsevier.* ISBN: 9780123919274.

[11] Atkins P. and de Paula, J. (2009) Physical Chemistry, 9th Edition. *Oxford University Press*, ISBN: 1429218126.

[12] Kirby, B. J. & Hasselbrink, E. F. (2004). Zeta potential of microfluidic substrates: 1. Theory, experimental techniques, and effects on separations. *Electrophoresis.* **25**(2), 187-202.

[13] Dörfler, H.-D. (2002). Grenzflächen und kolloid-disperse Systeme. *Springer-Verlag*, ISBN: 3540425470.

[14] Fritz, G., Schädler, V. Willenbacher, N. & Wagner, N. J. (2002). Electrosteric Stabilization of Colloidal Dispersions. *Langmuir*. 18, 6381–6390.

[15] Kim, D., Jeong, S. & Moon, J. (2006). Synthesis of silver nanoparticles using the polyol process and the influence of precursor injection. *Nanotechnology.* **17**(16), 4019-4024.

[16] Desai, R., Mankad, V.,Gupta, S. K., and Jha, P. K. (2012). Size Distribution of Silver Nanoparticles: UV-Visible Spectroscopic Assessment. *Nanosci. Nanotechnol.* **4**(1), 30-34.